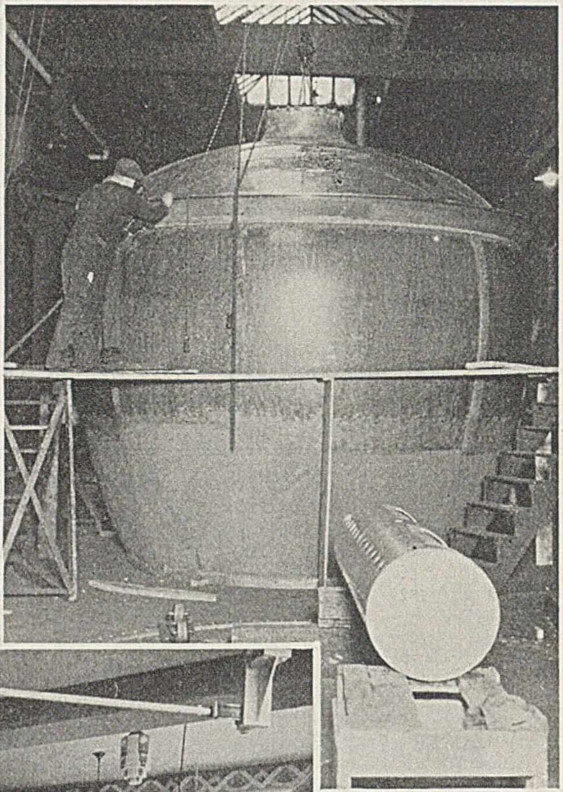
DISTILLERY WASTES

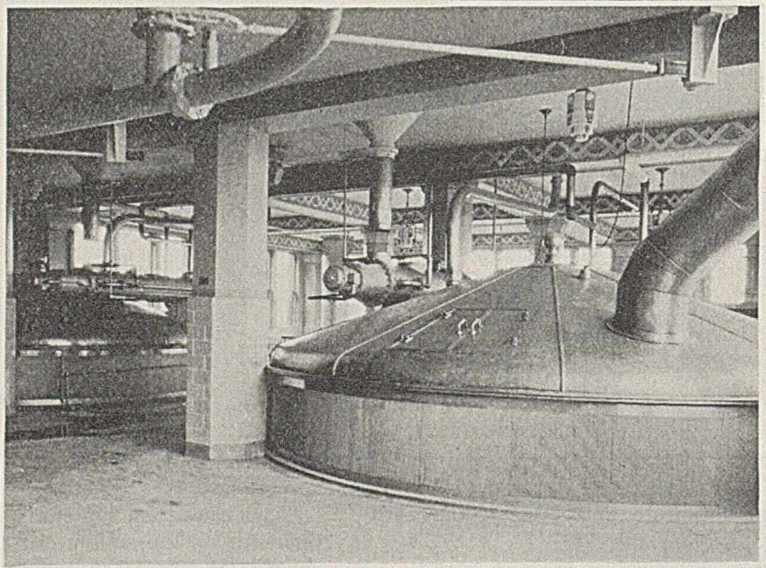
Chemical and Filtration Studies

C. R. HOOVER AND F. K. BURR

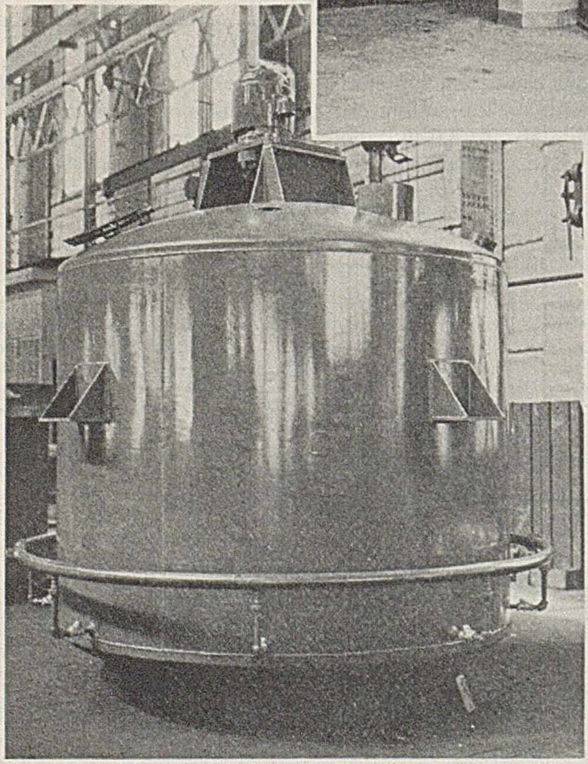
Wesleyan University and The State Water Commission of Connecticut, Middletown, Conn.



(*Upper*) A 350-Barrel Brew Kettle in the Process of Construction



(*Center*) Two of the 400-Barrel Mashing Machines Used by the Brewing Corporation of America



(*Lower*) A Cereal Cooker of Conventional Type

Courtesy, Buffalo Foundry and Machine Company

WASTES from distilleries, breweries, and alcohol plants constitute an increasingly important industrial and sanitary problem. These wastes are characterized by a very high content of oxidizable organic material. They may be described as the residues from the first distillation of the fermented primary materials, molasses, grains, tubers, fruits, and fruit juices, and are called "distillery slops," "beer slops," or "still bottoms." The most obvious impurities in such wastes are the suspended solids derived from grains. This material in most cases can be collected by screens, filters, or centrifuges, and moreover is rarely more than 50 per cent, and in some cases less than 1 per cent, of the content of dissolved matter. It is this large amount of dissolved matter—proteins, fats, gums, unfermentable sugars, and inorganic compounds—that constitutes the major waste disposal problem. Partial results of analyses of typical composite samples used in this investigation, are listed in Table I. Samples as much as 50 per cent more concentrated were sometimes used.

TABLE I. TYPICAL DISTILLERY WASTE COMPOSITES (IN P. P. M.)

	Spirit Type, pH 4.1	Bourbon Type, pH 4.3	Molasses, pH 4.5	Apple Brandy, pH 3.75
Total solids	47,345	37,388	71,053	18,866
Fixed solids	4,045	3,162	15,364	1,918
Volatile solids	43,300	34,226	55,689	16,948
B. O. D.:				
5-day	34,100	26,000	28,700	21,000
20-day	38,750	32,200	45,000	23,500
Oxygen consumed	14,280	17,790	29,747	9,070
Suspended solids	24,800	17,900	40	50
Acidity total	2,120	2,054	4,500	3,600

A number of investigators have proposed methods of treating distillery wastes. Because of the nature and content of such wastes, the possibilities of the recovery of by-products of value appear promising; in addition to stock feeding, two such recovery methods appear to be available—evaporation process, with or without incineration, for the recovery of potash (*1A*), and anaërobic fermentation methods at ordinary or elevated temperatures with the recovery of combustible gases (*2*). The usual simpler processes of treatment have, in general, been reported as unsuccessful in this country. However, most of these attempts have been made on the undiluted wastes. Abroad greater success has been observed (*4*). This article reports some results of two of the generally applicable industrial waste treatment processes, chemical precipitation and intermittent filtration.

Chemical Treatment

The following coagulants, neutralizing reagents, and conditioning reagents were tested in glass cylinders with mechanical and air stirring, and at different temperatures: lime, lime and ferrous sulfate, lime and ferric sulfate and chloride, lime and aluminum sulfate, sodium carbonate (alone and with the coagulants mentioned), lime and chlorine, lime and sulfur dioxide, sodium carbonate and chlorine; trisodium phosphate, clay, and diatomaceous silica alone and in combination with lime and coagulants. The effect of variation of the pH of mixtures was observed where this variable was affected by the reagents employed. Many of the coagulants tested did not produce appreciably greater decrease in oxidizable organic matter than simple sedimentation or filtration. Typical examples of tests, producing more than 10 per cent improvement over sedimentation, are shown in Table II. In this and subsequent tables and in the discussion the usual abbreviations—O. C. for oxygen consumed, B. O. D. for biochemical oxygen demand, and p. p. m. for parts per million—are used.

All tests made point to the conclusion that treatment of undiluted wastes of grain types containing suspended matter requires from 20 to 55 pounds per thousand gallons of the usual chemical coagulants, and produces, after standing 1 hour, a sludge occupying from 40 to 74 per cent of the volume of the original waste. The sludge produced filtered more readily than the original suspended matter but was not appreciably decreased in volume. While only oxygen-consumed values are given in Table II, the percentage decrease in biochemical oxygen demand has been determined in a sufficient number of tests to establish the fact that the percentage reduction is substantially equal. The 5-day biochemical oxygen demand of the clear effluent from grain wastes was, in the best tests, approximately 60 per cent less than in the original waste, but the maximum reduction in dissolved oxidizable material observed, with relatively clear wastes, was only 22 per cent.

TABLE II. CHEMICAL TREATMENTS OF DISTILLERY WASTE

Influent No.	Influent pH	O. C.	Treatment	Effluent pH	Effluent O. C.	Sludge, 1 Hr.	Reduction in O. C.
		P. p. m.	*Lb./1000 gal.*		*P. p. m.*	*Per cent*	
			Grain Type				
1	4.3	19,400	Lime 20	8.5	7,040	50	64
2	4.3	19,400	Lime 25, ferric sulfate 25	7.4	8,020	70	59
3	4.3	19,400	Lime 30, ferric chloride 25	8.0	5,050	75	74
4	4.3	17,970	Lime 26, sulfur dioxide 13	6.0	10,352	60	42
			Diluted Grain Type				
5	4.4	2,220	Lime 2	7.2	1,340	15	40
6	4.4	2,220	Lime 5, copperas 3	8.0	1,263	15	43
7	4.4	2,220	Lime 1.5, ferric sulfate 3	4.2	1,103	14	50
8	4.4	2,220	Lime 4, ferric sulfate 3	6.9	973	15	56
9	4.4	2,220	Lime 2, ferric chloride 3	5.1	834	15	62
			Clear Wastes				
10	3.5	18,060	Lime 20	5.3	16,306	2	10
11	3.5	18,060	Lime 40	7.2	15,720	5	13
12	4.0	17,240	Lime 20, alum 10	6.7	15,410	10	11
13	4.0	17,240	Lime 20, ferric sulfate 5	6.6	15,100	10	12
14	4.0	17,240	Lime 40, ferric sulfate 25	8.2	13,680	35	21

This was accomplished with 25 pounds of ferric chloride and 40 pounds of lime per thousand gallons and would appear to involve a chemical cost out of proportion to the benefit secured.

The disposal of an increased weight of suspended material is imposed by chemical treatment bringing about the largest decrease in dissolved substances. Chemical treatment of diluted waste increased the total volume, as well as weight, of sludge formed, and offers no economy in amount of chemical required. Furthermore, the solids removed with strong chemical treatment, while usable, are naturally less desirable for cattle food than untreated solids. Hence, we conclude that chemical treatment alone is of little value in disposing of distillery wastes, but as a preliminary step in other processes, as will be mentioned later, such treatment may have some value.

Filtration

Three types of filters were used in this investigation: (*a*) lath-grid trickling filters (*3*), shown in Figure 1; (*b*) intermittent sand filters, constructed of lengths of hubbed sewer tile cemented together; and (*c*) coke breeze intermittently fed filters, similar in construction to the sand filters. Coke and coke breeze ballast was also used in the trickling filter shown in Figure 1.

Preliminary investigation indicated that grave difficulties were involved in applying grain type wastes, carrying sus-

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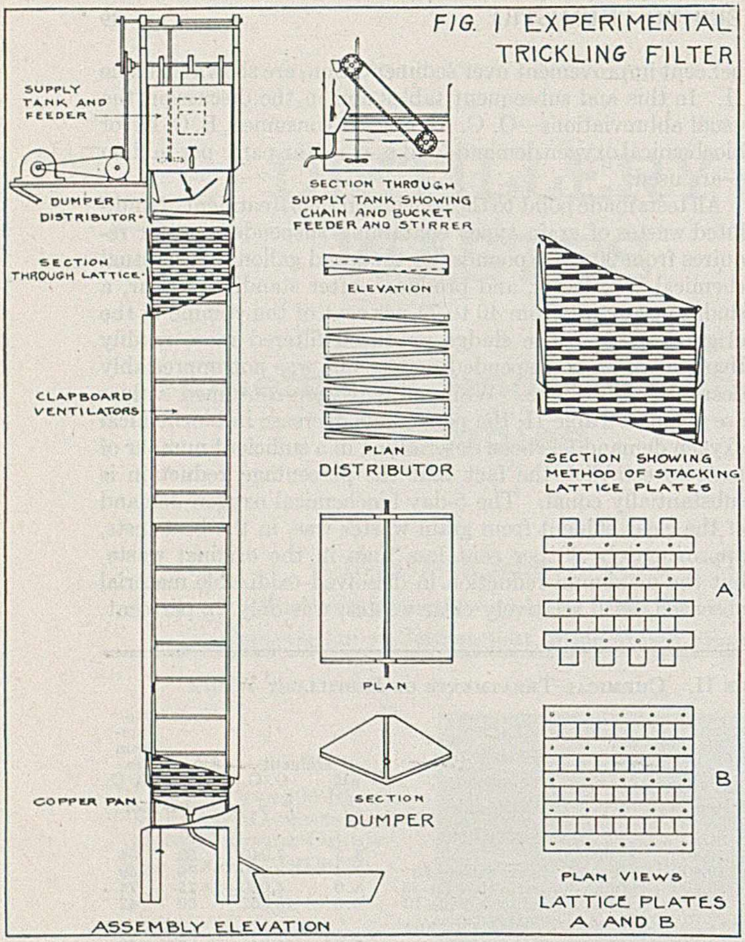
Chemical treatment of distillery wastes with the ordinary coagulants does not offer advantages commensurate with the expense involved. Clarified grain-type distillery wastes and relatively clear apple-brandy or molasses-alcohol wastes, when diluted to a content of oxidizable material not in excess of 2000 p. p. m. B. O. D., are reduced 90 per cent in B. O. D. value by passing through a 10-foot-deep trickling filter at the rate of 1,000,000 gallons per acre per day. Applied wastes of similar strength are reduced 98 per cent when passed through a 4-foot-deep intermittent filter of coke breeze at the rate of 200,000 gallons per acre per day.



pended matter, to sand or coke breeze filters; consequently, a series of laboratory filtration tests were run with Büchner funnels and confirmed by filtration on a small Oliver filter, in an effort to clarify such wastes. Conditioning was found to be necessary for successful continuous filtration. Eleven pounds of a commercial grade of ferric sulfate and 15 pounds of lime per thousand gallons increased the filterability approximately ten times at a temperature of 60° C. The pH for optimum filterability was found to be 7.9 and above.

Using a small Oliver-type vacuum filter, the results with various types of filter cloths indicated preference for soft nap fabrics when unscreened wastes were used, and close woven muslin for the more gelatinous screened wastes. Filtration rate increased with rise in temperature up to the point where boiling of the filtrate began to complicate operations. Conditioning with 10 pounds of ferric salts and 15 to 25 pounds of lime per thousand gallons produced the best results observed, but 20 pounds of lime alone appeared to be satisfactory. With such conditioning, at 60° C. (140° F.) a filter cake containing 71 per cent of moisture was obtained from an unscreened spirit-type waste. The total and volatile solids were reduced from 64,370 and 46,975 p. p. m. to 18,026 and 14,429 p. p. m., respectively.

Trickling Filters

Figure 2 illustrates typical results with a diluted, filtered, spirit-type waste, conditioned by lime to a pH of 6.8–7 before filtering. The new lath-grid filter used was washed with water, drained for 24 hours, dosed once with supernatant liquid from stale sewage, and again allowed to drain 24 hours. The rate of dosage averaged 216,000 gallons per acre per day for the first 16 days, and then 460,000 gallons per acre per day.

Table III gives the effect of variations in the rate of dosage and concentration of applied waste. The waste used was diluted brandy "still bottoms." After a trickling filter had become active, it was found unnecessary to neutralize the applied waste. In fact, a slightly better O. C. reduction was secured by using an acid influent.

Table III. Effect of Rate of Dosage and Concentration of Waste on Apple Brandy Still Bottoms through a Trickling Filter

Time	O. C. of Applied Waste	Rate of Dosage	Reduction in O. C.	Time	O. C. of Applied Waste	Rate of Dosage	Reduction in O. C.
Days	*P. p. m.*	*Gal./acre/day*	*Per cent*	*Days*	*P. p. m.*	*Gal./acre/day*	*Per cent*
1	764	238,500	88	30	654	642,000	92
7	762	238,500	90	31	1521	348,000	89
9	762	525,000	91	36	1521	348,000	89
14	686	525,000	91	37	1484	642,000	85
15	686	926,000	88	42	1484	642,000	88
17	686	1,095,000	88	43	1471	1,095,000	86
19	686	1,095,000	87	48	1471	1,095,000	88
20	676	1,260,000	87	50	2693	890,000	84
24	676	1,260,000	85	55	2809	890,000	77
25	654	642,000	88	60–90	Av. 1460	Av. 1,045,000	88

The retention time of the filter during these tests was determined to be 51 minutes at 600,000 gallons per acre per day, with hourly dosing cycles. With side and bottom ventilation a 20-minute dosing cycle appeared to be most efficient, but with top ventilation only, 45- to 60-minute cycles produced the best results. O. C. reductions were decreased about 5 per cent when bottom and side ventilation were eliminated. A small amount of well-stabilized suspended matter was periodically found in the effluent.

Samples taken at different depths, during the operation of the trickling filter, indicated that over 90 per cent of the action occurred in the first 5 feet and 98 to 100 per cent in the first 6 feet with the maximum rate of dosage.

The O. C. values, given in Figure 2, Table III, and subsequent figures were obtained with a permanganate solution ten times as strong as the standard method (*1*). Comparison with biochemical oxygen demand values indicates that the ratio of 5-day B. O. D. to recorded O. C. was 1.4. All other determinations were made in accordance with the standard methods (*1*). These tests, therefore, indicate that a filtered or clear distillery waste, diluted to 2000 p. p. m. B. O. D., will lose approximately 90 per cent of its oxidizable material when subjected to trickling filtration at rates not exceeding one million gallons per acre per day.

Sand Filters

Intermittent sand filters have been extensively tested with numerous industrial wastes, other than diluted distillery wastes (*5*). The experimental sand filters used in this investigation were 4 feet deep and had a small amount of bottom ventilation. The filters were dosed in from 1- to

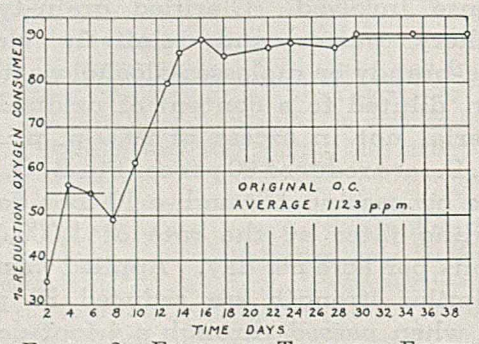


Figure 2. Effect of Trickling Filter Treatment of Filtered Spirit-Type Waste

4-hour cycles at rates of from 50,000 to 100,000 gallons per acre per day. The sand used was washed sea sand or sand from active sanitary-waste filter beds, and had an effective size of 0.2–0.3 mm. (0.0079–0.0118 inch) and a uniformity coefficient of from 10 to 20. Wastes applied were either filtered, sedimented, or prefiltered through 1 foot of washed coke breeze having an effective size of 0.5 mm. (0.0197 inch) and a uniformity coefficient of 60. Permanent clogging that necessitated removing all of the sand, which condition apparently could not be prevented by periodic raking and washing, resulted from apple brandy wastes in periods of from 4 to 7 months at average rates of 100,000 gallons per acre per day. Figure 3 shows a summary of the log of the most successful run of any intermittent sand filters with the types of distillery wastes tested. Dosage was at the uniform rate of 100,000 gallons per acre per day for 5.5 days of each week. Nitrification, apparently, did not begin for over 3 months. The reduction in O. C. is the total effect of pretreatment and filtration; it was checked occasionally by B. O. D. determinations and, as previously stated, showed approximately 40 per cent greater values in p. p. m. but substantially the same percentage reduction.

The persistent clogging and low capacity of these sand filters led to tests of other materials, having greater porosity but able to produce reductions higher than those obtained with trickling filters.

Coke-Breeze Filters

Observations on the coke-breeze prefilters, used with sand filters, showed that they made a contribution to the total reduction of oxidizable matter and that they did not clog readily. Coke breeze was therefore substituted for sand. The coke used was the commercial breeze from a by-product coke-oven plant. It was subjected to a washing process, similar to that in a sand washer, which resulted in removing the fine dust but did not decrease the original volume. The effective size of the washed material was 1 mm. and the uniformity coefficient 10. Results with these coke-breeze filters have been satisfactory with relatively clear wastes. One 4-foot-deep filter was run for approximately a year at 200,000 gallons per acre per day, 5.5 days a week. Following the 12-month run, the filter was well washed and was then operated for 7 months with a coke-breeze prefilter on a waste which contains approximately 1 per cent of settleable solids.

Figure 4 gives a typical log summary of a coke-breeze filter to which a 1:9 dilution of apple brandy waste was applied. The waste averaged approximately 1500 p. p. m. O. C. or the equivalent of 2100 p. p. m. 5-day B. O. D. The average pH's of influent and effluent were 3.9 and 7.9, respectively. The usual rate of dosage during this run was 200,000 gallons per acre per day but this has been increased at times to as high as 500,000. One- to four-hour dosing cycles have been used.

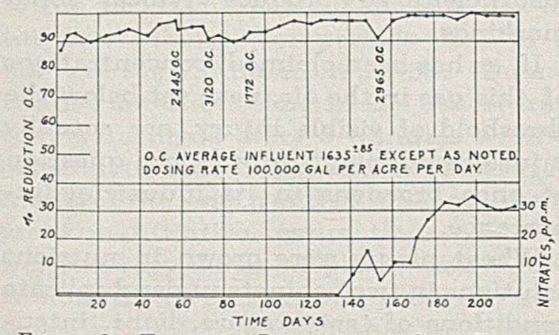


Figure 3. Effect of Intermittent Sand Filter, 4 Feet Deep, on Oxygen Consumed and Nitrates of Apple-Brandy Still Bottoms

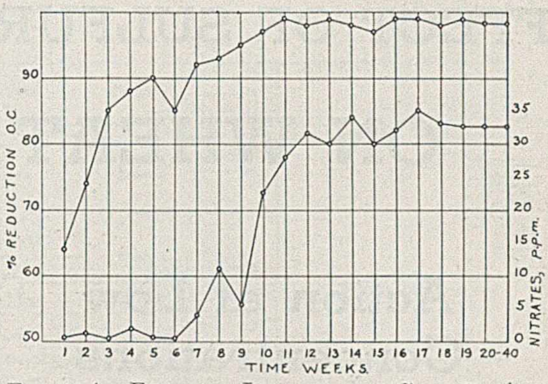


Figure 4. Effect of Intermittent Coke-Breeze Filter, 4 Feet Deep, on Oxygen Consumed and Nitrates of Apple-Brandy Still Bottoms

Coke filters wash readily. Flooding apparently loosens the whole bed of the filter because of the low density of the coke particles. The filters started promptly when well washed, special inoculation being found unnecessary. Sewage or sludge extract was used if filters did not begin to function after being dosed once and allowed to stand from 24 to 48 hours.

Prefilters become clogged after a few months of use if they are of small area in proportion to the filter area, but they wash well and the ballast can also be disposed of by using as fuel. The retail cost of coke breeze at one coke plant in New England is $2.75 per ton with a truck delivery cost of 3 cents per ton-mile. On the basis of the removal of organic matter secured in these tests, the cost of the coke-breeze ballast for the removal of 1 pound of organic solids per day would be approximately $5.00 within a radius of 50 miles of the source of coke.

The effect of temperatures above 30° C. (86° F.) was not investigated, but no noticeable change in efficiency of the operation of any filter was noticed over the temperature range of 18° to 30° C. (64.4° to 86° F.). Insects (apparently a type of sewage fly) were noticed in small numbers over filters on the surface of which solid matter accumulated, but such flies were not observed over filters to which clarified wastes were applied.

Acknowledgment

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